



Amineborane-Based Chemical Hydrogen Storage

Department of Chemistry
University of Pennsylvania

DOE Chemical Hydrogen
Storage Center of Excellence

2008 DOE Hydrogen Program Review

June 10, 2008

Project ID: **ST7**

This presentation does not contain any proprietary or confidential information

Project Overview

Timeline

Project Start: FY 2005
Project End: FY 2009
Percent complete: 70%

Budget

Total Project Funding: \$1,783,787
DOE: \$1,417,353
Penn: \$366,434

DOE Funding in 07: \$275,000
DOE Funding in 08: \$300,000

Barriers Addressed

Barriers

- A. System Weight and Volume
- B. System Cost
- E. Charging/Discharging Rates
- R. Regeneration Processes

Targets

DOE storage targets for kg-H₂/kg, kWh/L and \$/kWh

Collaborators on Amineborane Project



Overall Project Objectives and Approach

Overall Center and Project Objectives

- Develop Methods for On-Demand, Low Temperature Hydrogen Release from Chemical Hydrides that Can Achieve DOE Targets
- Develop High Conversion Off-Board Methods for Chemical Hydride Regeneration

In collaboration with Center Partners, the goal of this project is to develop new methods for **Hydrogen-Release** and **Regeneration** that will enable the use of amineboranes for chemical hydrogen storage.



Penn Project Approaches to Amineborane Hydrogen-Release and Regeneration Goals

Hydrogen-Release: Use the activating effects of ionic liquids, chemical promoters and/or metal-catalysts to enhance the rate and extent of hydrogen release from amineboranes.

Regeneration: Goals of Penn off-board BNH_x regeneration approach: (1) high yields; (2) avoid formation of B-O bonded intermediates; (3) avoid formation of hazardous diborane; (4) recover all products. Penn method converts BNH_x to boron trihalides, which are then converted to AB via sequential coordination, reduction and displacement reactions.

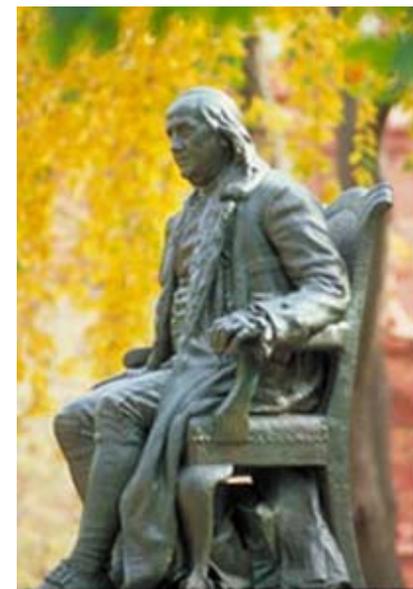
2008 Objectives and Achievements

Penn Objectives for the Last Year

- Significantly increase the rate and wt% of AB H₂-release.
- Learn how to better control AB H₂-release mechanisms, intermediates and final spent fuel products.
- Further optimize the super-acid/halide-reduction regeneration process.

Summary of Penn Achievements Since Last Review

- A greatly increased rate of H₂-loss (~2.3 eqv. in 15 min) with 10.2 mat-wt% from AB/ionic-liquid mixtures was achieved at 120°C.
- A rhodium catalyzed AB H₂-release in an ionic liquid was demonstrated that increases the loss rate for the first H₂ eqv.
- Proton sponge in ionic liquids was shown to both increase the release rate of the second AB H₂ eqv. and greatly reduce foaming.
- NMR, DSC and rate studies revealed that while there are different mechanistic pathways for AB H₂-release, the final spent fuels all contain trigonal sp² BNH_x structures thus enabling a common regeneration strategy.
- New high yield processes for the conversion of BX₃ to AB were developed that avoid the formation of hazardous diborane and allow complete separation and recovery of all products.



Penn Research Team

PI: Larry Sneddon

Postdoctoral: Laif Alden

Students:

Dan Himmelberger

Bill Ewing

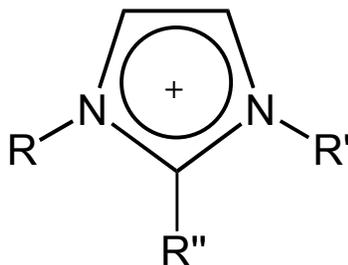
Penn Approach to Improving Ammonia Borane H₂-Release. Increase the Rate and Amount of H₂-Release by Activation of AB with:

- 1. Ionic Liquids**
- 2. Metal-Catalysts/Ionic-Liquids**
- 3. Chemical Promoters**

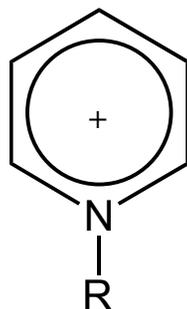
1. Why Ionic Liquid Solvents for Amineborane Dehydrogenations?

Ionic Liquid Solvents

Cations:



N,N'-imidazolium



N-pyridinium

Anions:

Reactive: AlCl_4^- , Al_2Cl_7^-

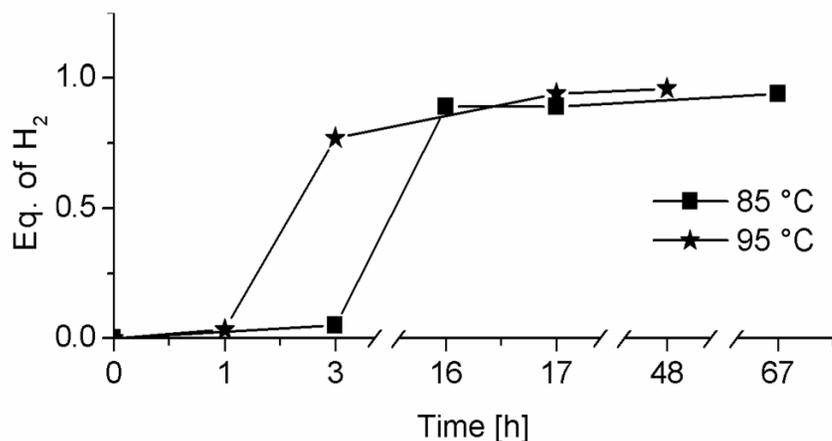
Inert: PF_6^- , BF_4^- , Cl^-

Advantages

- Negligible vapor pressures
- Dissolve both neutral and ionic species
- Thermally stable to elevated temperatures
- Non-coordinating anions and cations provide an inert, polar reaction medium
- **Promote the formation of ionic or polar intermediates and transition states**

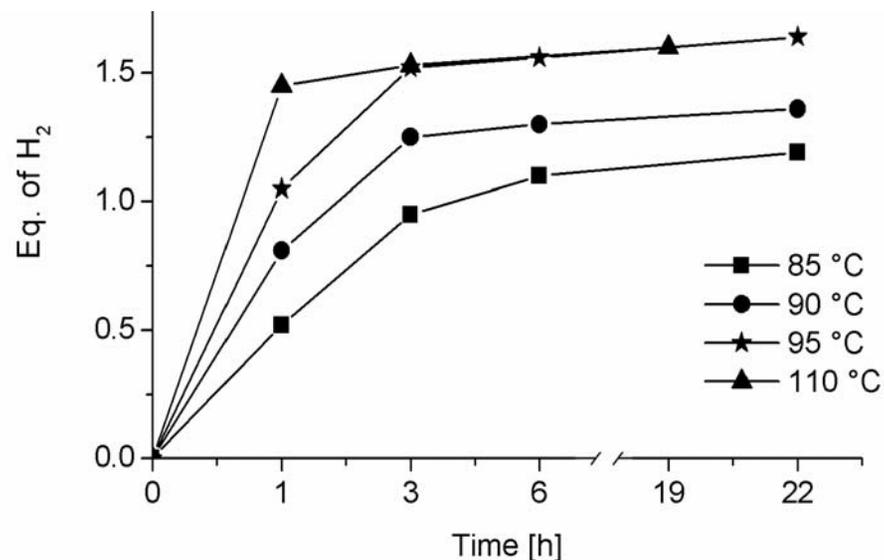
2006: Ionic Liquids Increase the Rate and Extent of H₂-Release from AB and Eliminates Induction Period

Neat NH₃BH₃



NH₃BH₃ + Ionic Liquid[‡]

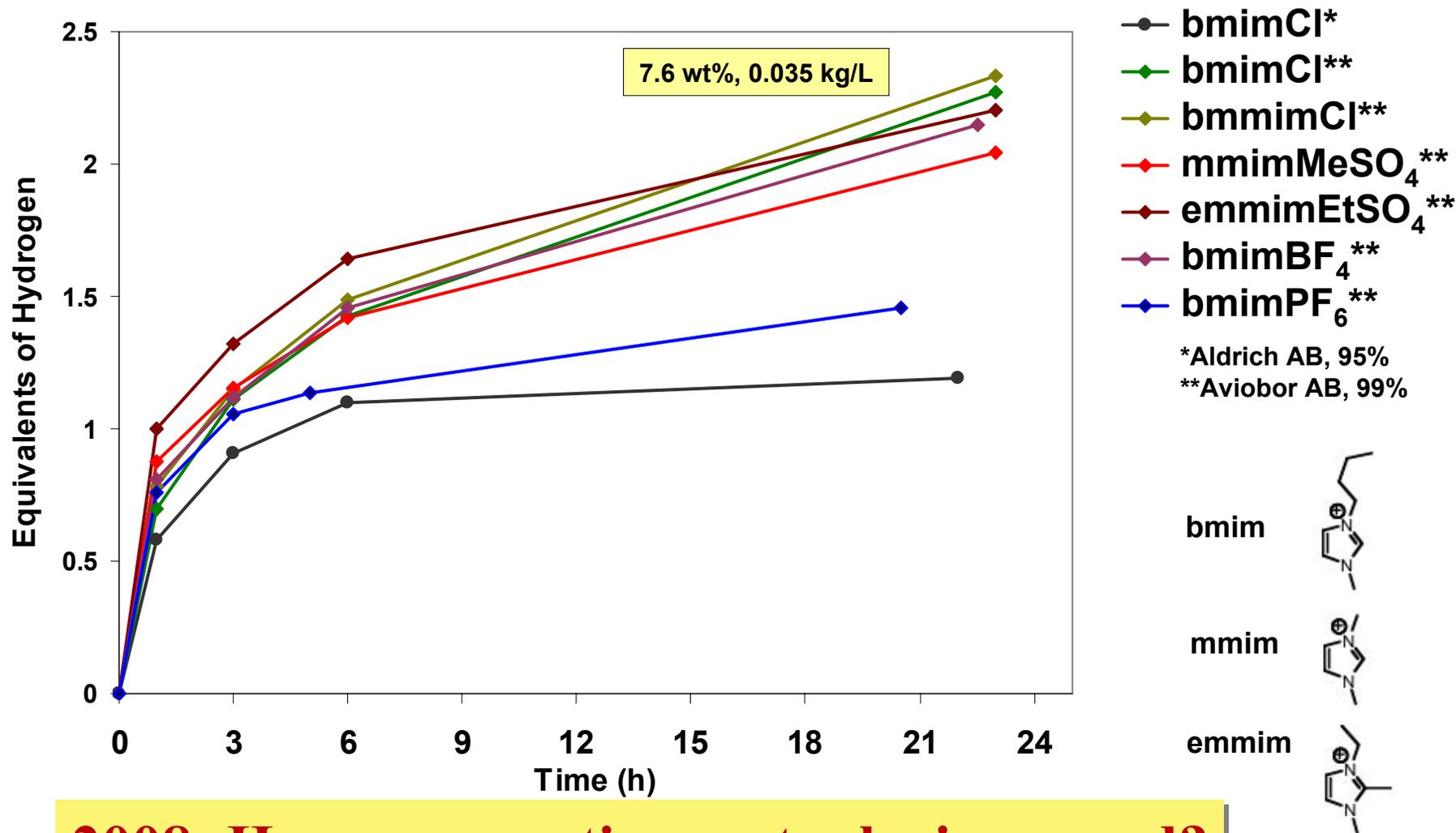
(50:50 wt% mixture)



[‡]1-Butyl-3-methylimidazolium chloride

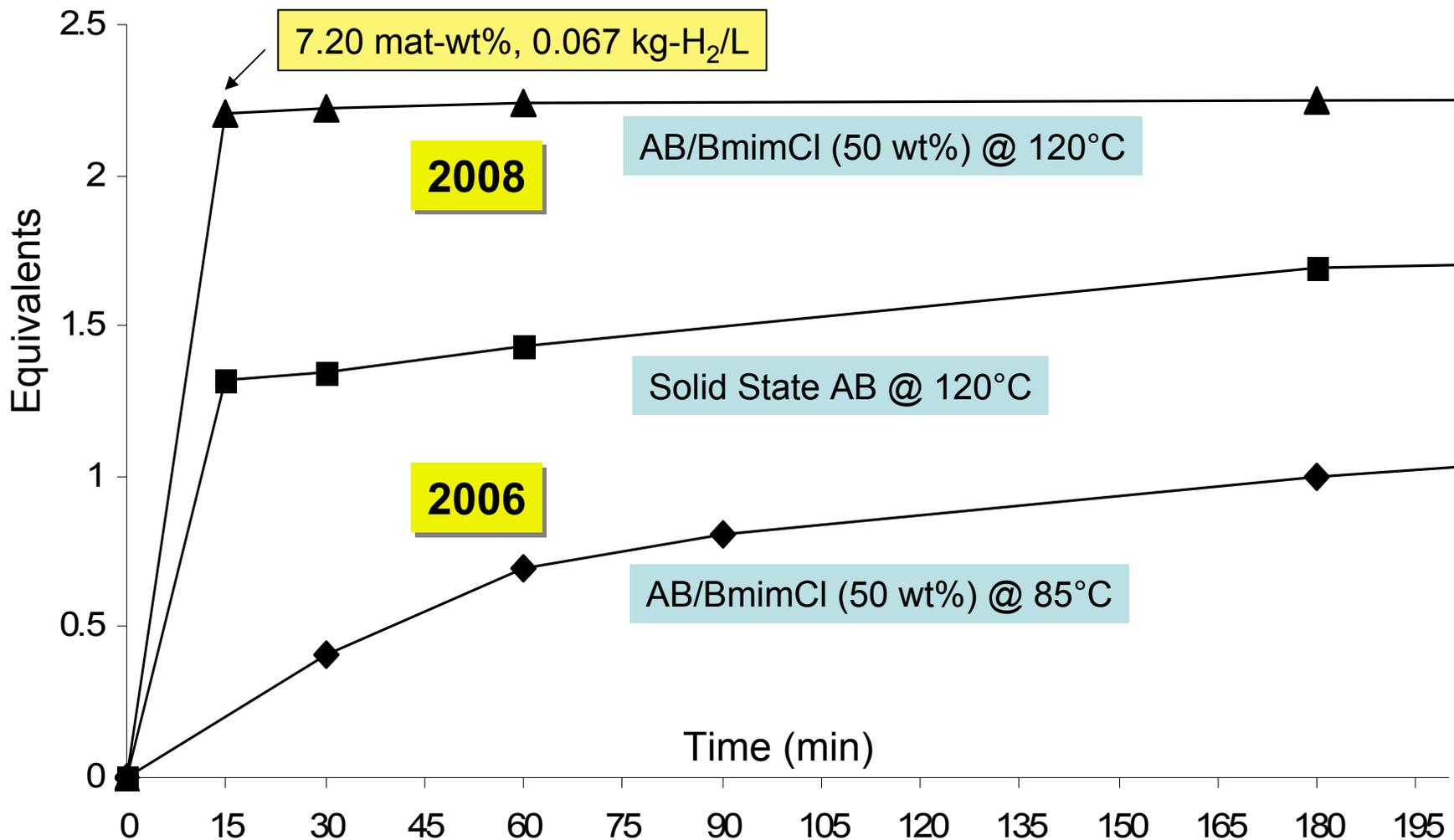
Bluhm, M. E.; Bradley, M. G.; Butterick, R.; Kusari, U.; Sneddon, L. G.
J. Am. Chem. Soc. **2006**, *128*, 7748-9.

2007: Other Ionic Liquids Show Increased Extent and Rate of H₂-Release at 85 °C



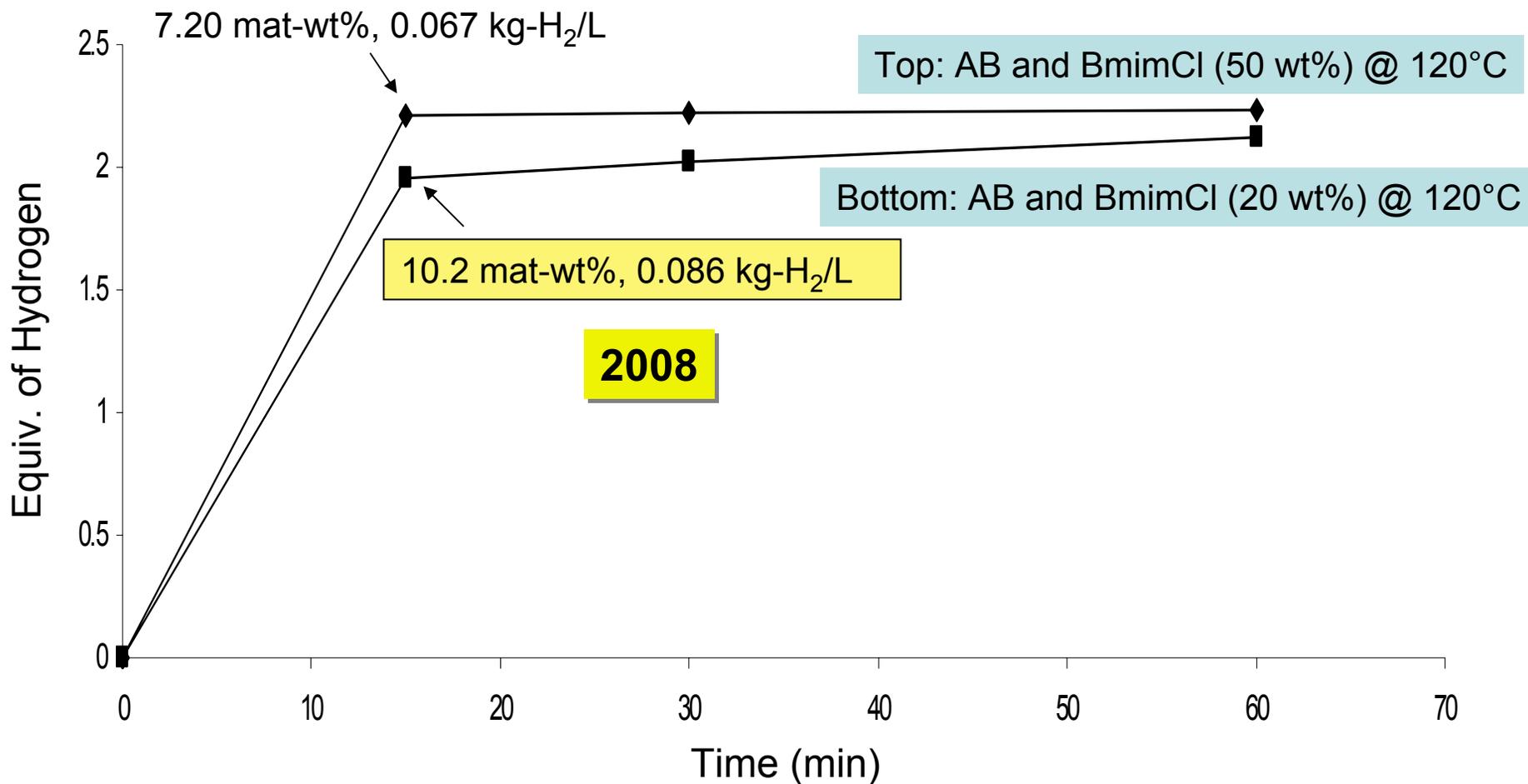
2008: How can reactions rates be increased?

2008: H₂-Release Rates of AB in Ionic Liquids are Greatly Increased at 120 °C



Similar H₂-Release Rates for 1st and 2nd Equivalents!

2008: 10.2 Mat-wt% H₂ in 15 min at 120 °C is Achieved When only 20% BmimCl is Used



2008: Metrics for New “Best” H₂-Release Systems

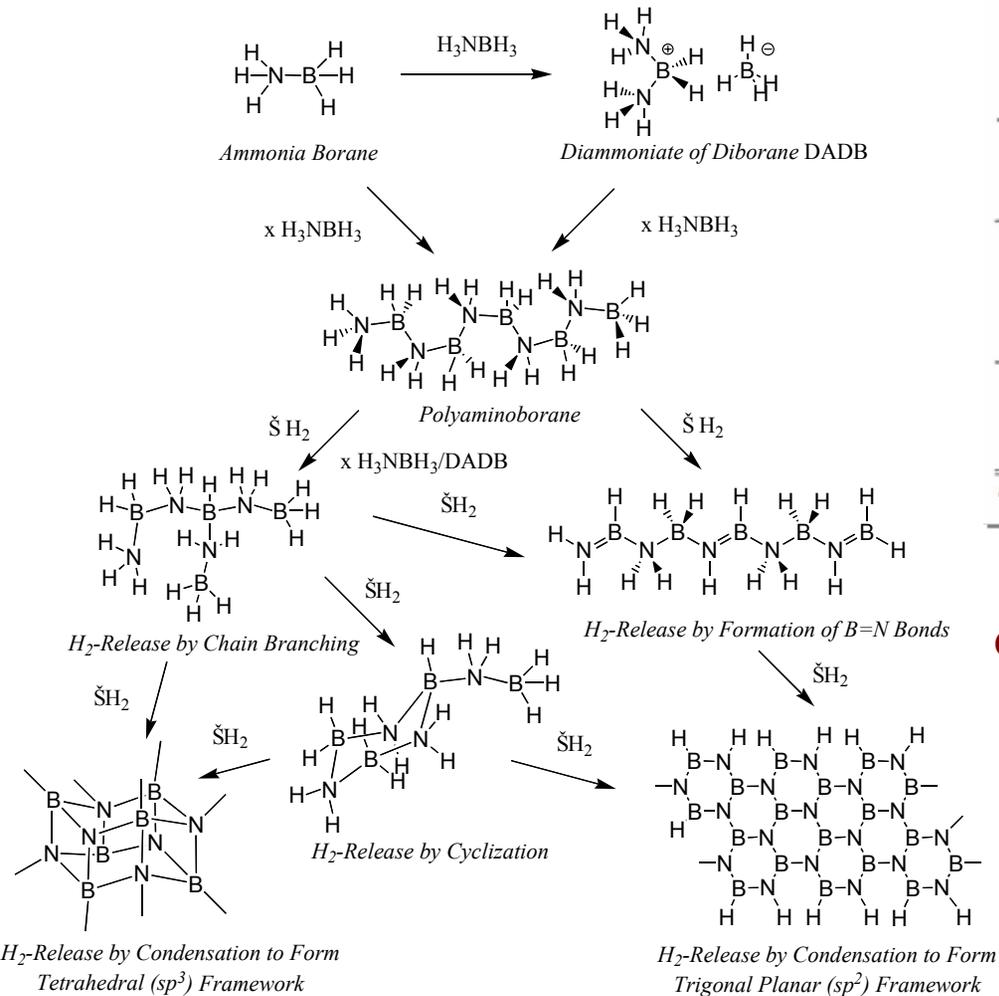
Metrics	AB Thermolysis at 120°C		
	Solution-State (15 min, ~2 Eq. H ₂)		
	50 wt% BmimCl	40 wt% BmimCl	20 wt% BmimCl
Grav. density (Mat. wt%)	7.2	8.7	10.2
Vol. density (Kg-H ₂ /L Mat.)	0.067	0.078	0.086
H ₂ Flow Rate (g/s) per kg Material	0.08	0.097	0.114
Kg of Mat. for 0.8 mol/sec	20	17	14

DOE Total System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)	Volumetric Density (Kg-H₂/L)
4.5 (2007), 6.0 (2010), 9.0 (2015)	0.036 (2007), 0.045 (2010), 0.081 (2015)

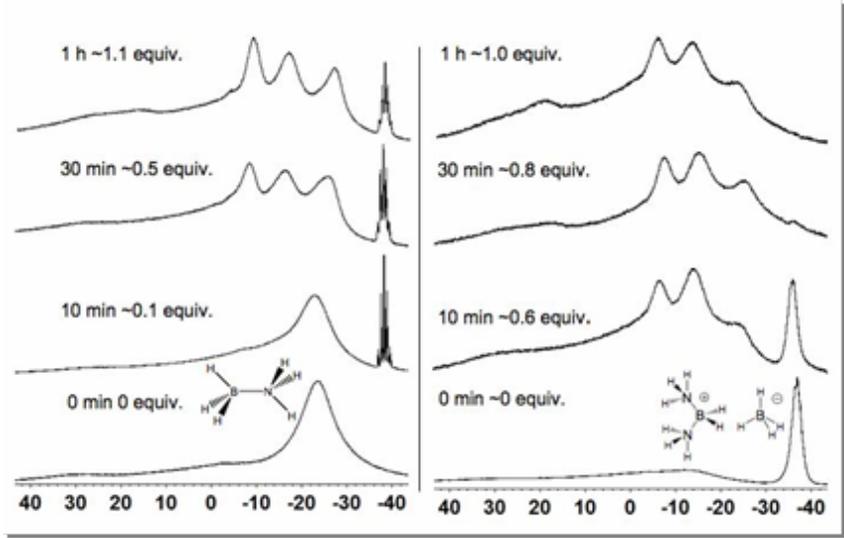
NMR Studies Identify Initial and Final Release Products

Possible Mechanistic Steps



Solution ¹¹B NMR

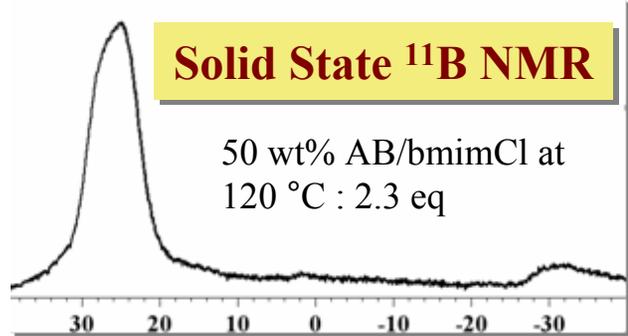
10 wt% AB and DADB in bmimOTf at 85°C



Conclusion: Both DADB formation and decomposition is enhanced in ionic liquids

Solid State ¹¹B NMR

50 wt% AB/bmimCl at 120 °C : 2.3 eq



Conclusion: Final Spent Fuel Product has sp²-type framework

2. Why Use Metal Catalysts for Amineborane Dehydrogenations in Ionic Liquids?

Catalysts in Conjunction with Ionic Liquids Could Provide:

- (1) Faster H₂-Release
- (2) Better Control of H₂-Release Rates
- (3) Lower Temperature Reactions
- (4) Synergistic Release Mechanisms

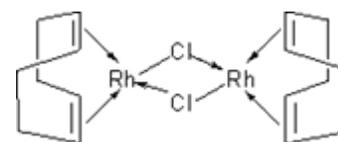
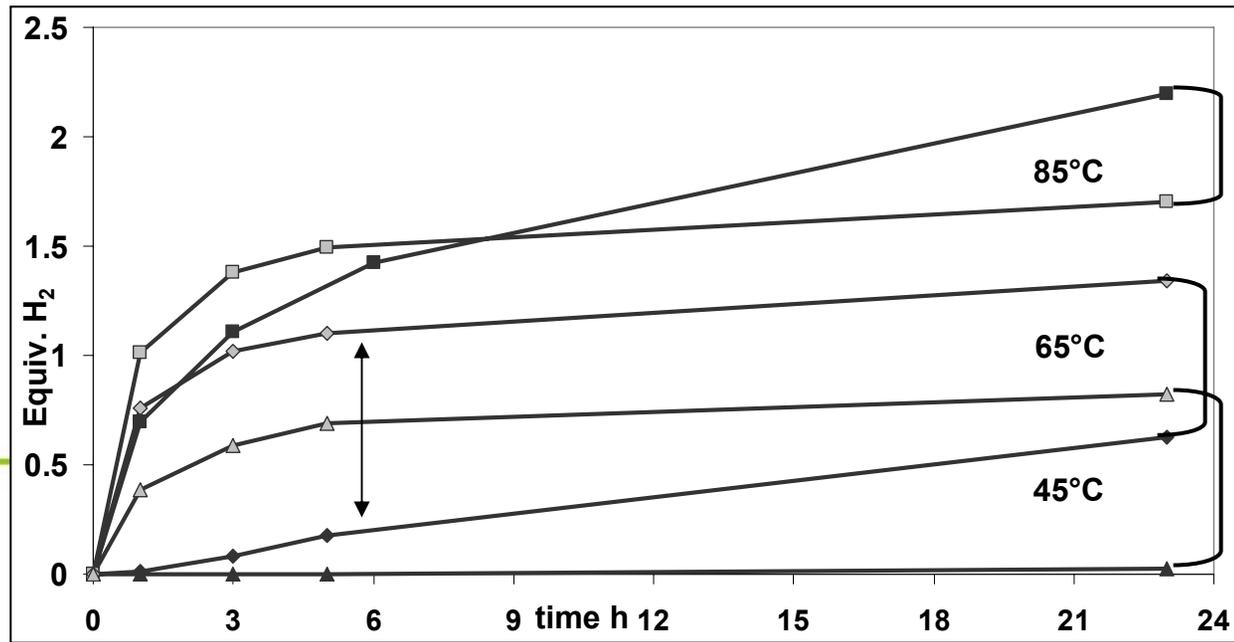
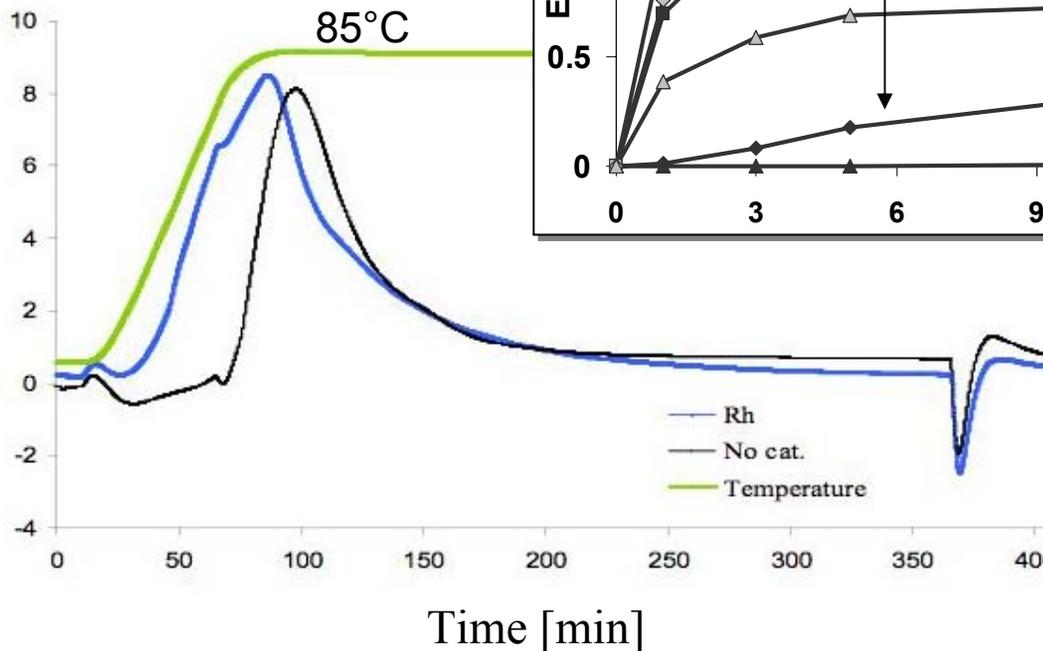
Center Partners (LANL and U Washington) have previously demonstrated metal catalyzed AB H₂-release in organic solvents.

Since the last program review, AB catalyzed H₂-release in ionic liquids has been achieved.

2008: Rh Catalyst Increases Release Rate of the First Equivalent of H₂ from AB in Ionic Liquids

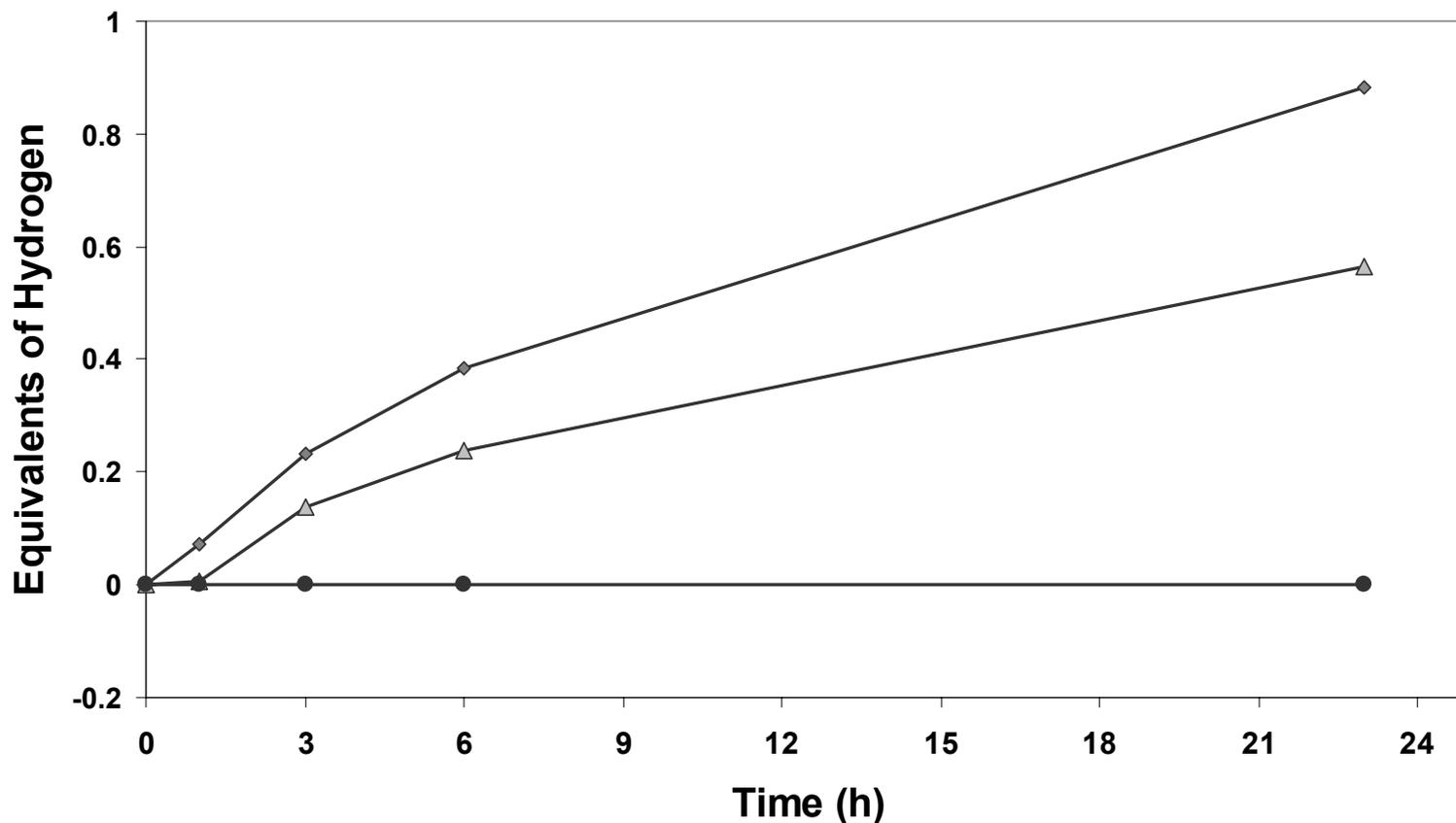
50 wt% AB
in bmimCl
5 mol% Rh

DSC



- 85°C
- ◆ 65°C
- ▲ 45°C
- ◻ 85°C w/ Rh
- ◊ 65°C w/ Rh
- ◀ 45°C w/ Rh

2008: Rh Catalyzes Dehydrogenation of Other Amineboranes in Ionic Liquids

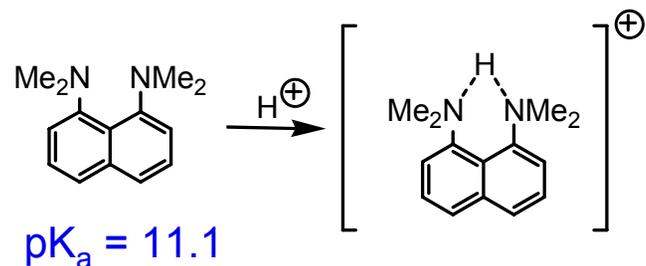
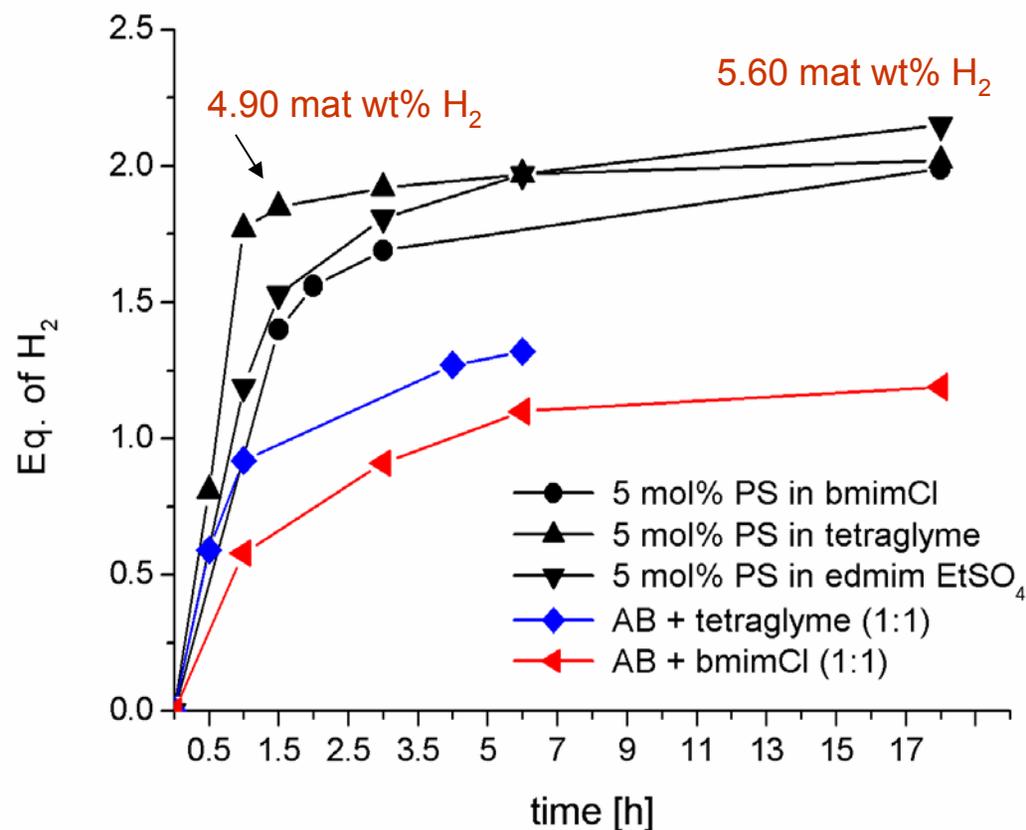


Me₂NHBH₃ (10wt%) in mmimMeSO₄ at 45°C

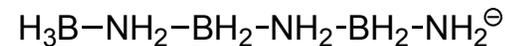
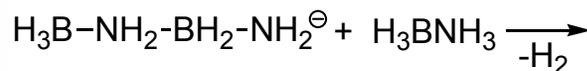
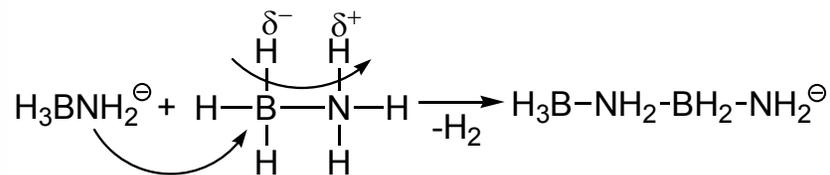
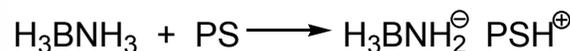
- △ 5 mol% Rh(COD)Cl
- ◇ 1 mol% Rh(COD)Cl
- 0 mol% Rh(COD)Cl

3. 2007: Chemical Promotors: Proton Sponge Increases H₂-Release from AB in Solution and Avoids the Formation of M⁺BH₄⁻ and NH₃

NH₃BH₃ + 5 mol % PS at 85 °C in Ionic-Liquids or Tetraglyme (250 mg) (91 mg)

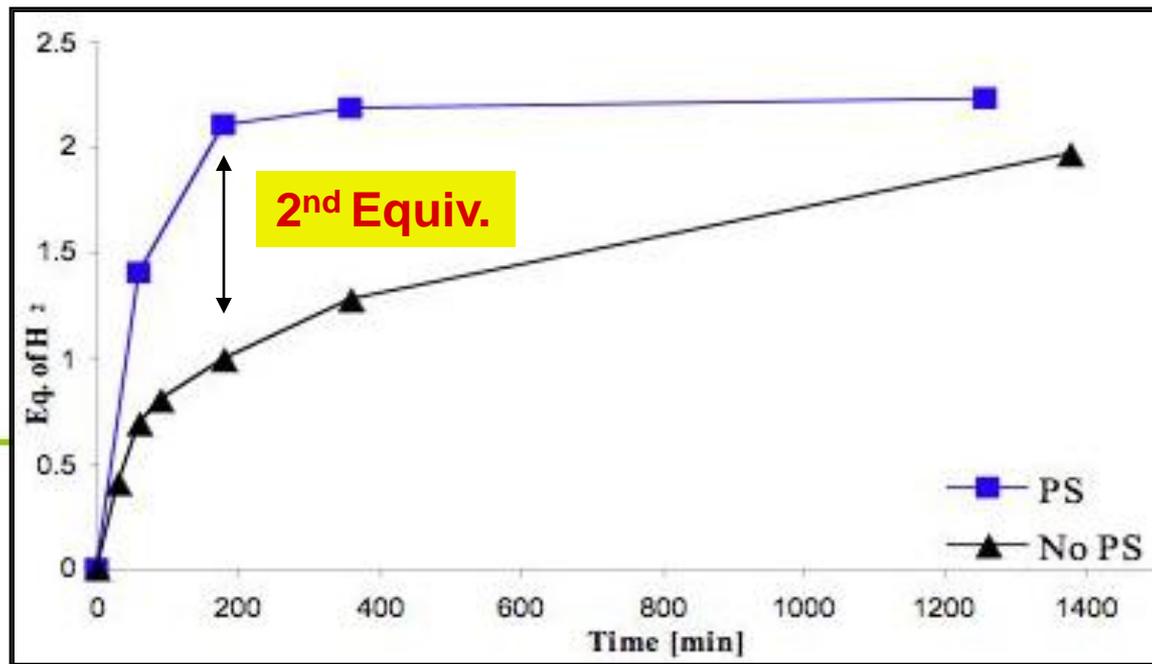
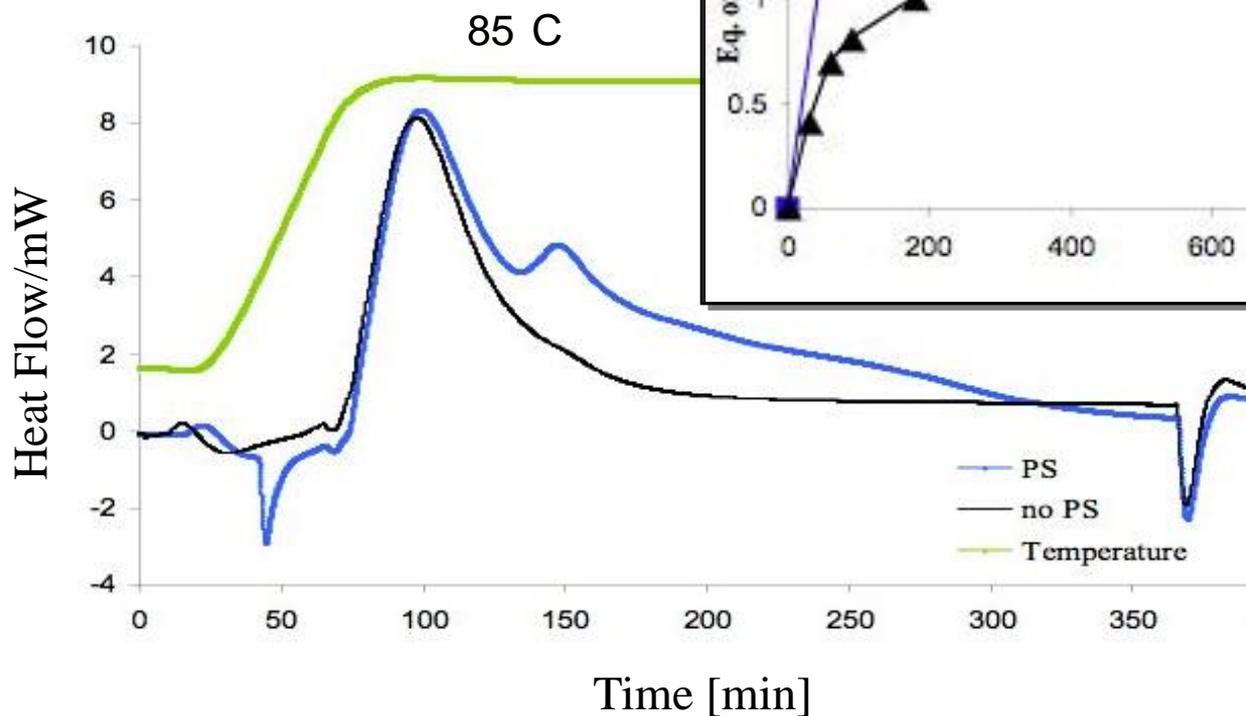


Proton Sponge Reaction Mechanism



2008: Proton Sponge Increases the Release Rate of the Second Equivalent of H₂ from AB and Reduces Foaming

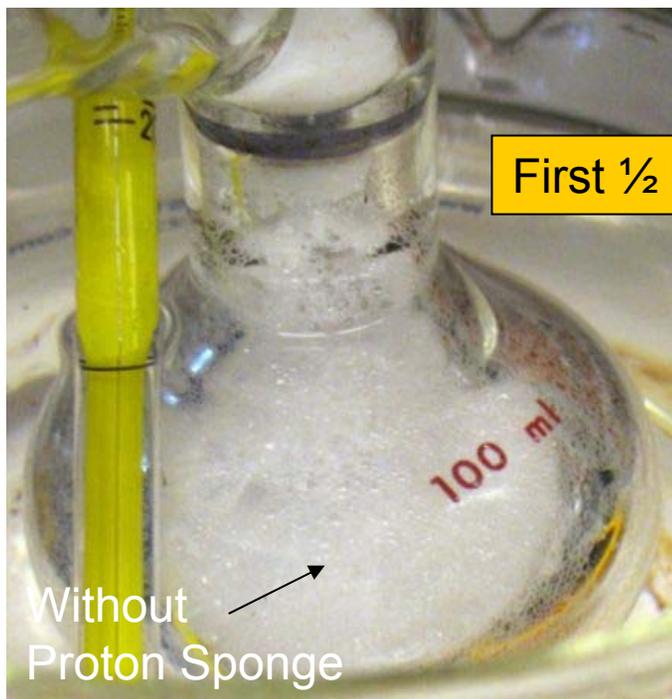
AB with 5 mol% PS
in bmimCl at 85 °C



2008: Foaming Suppressed with Proton Sponge



First ½ h of Reaction



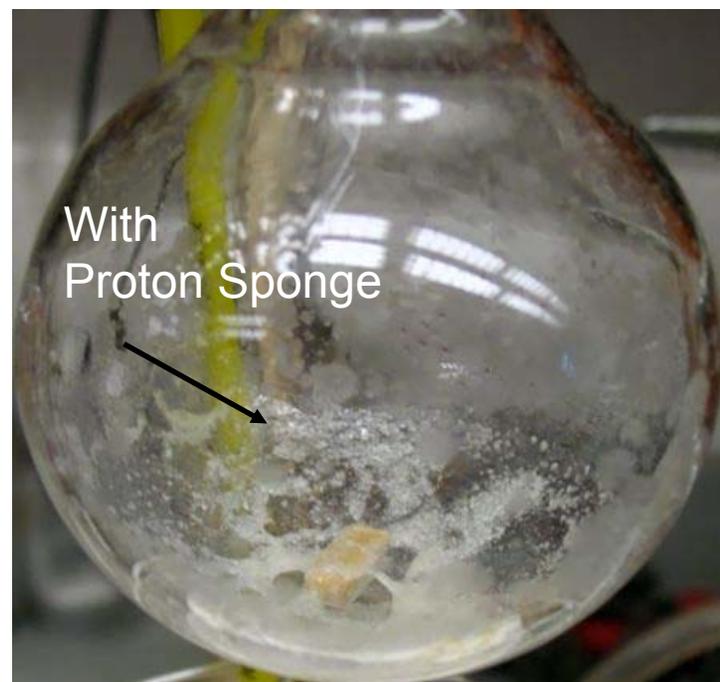
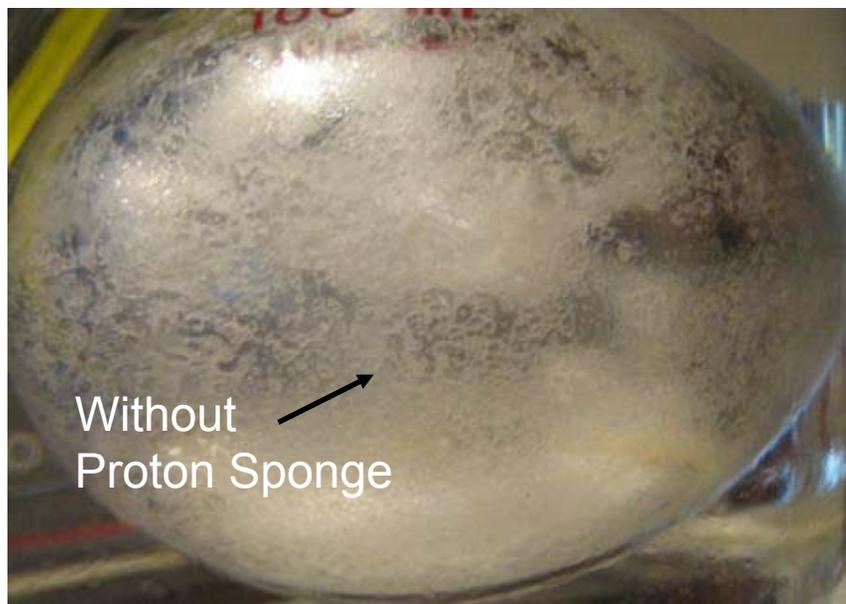
Without Proton Sponge

First ½ h, After H₂-Removed



With Proton Sponge

2008: Foaming Suppressed with Proton Sponge

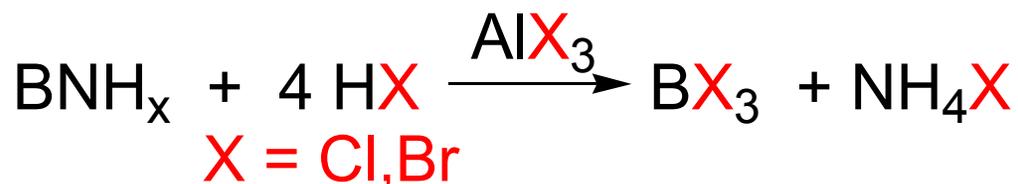


After 23 hours

Penn Approach to Regeneration: Super-Acid/Halide-Reduction Process

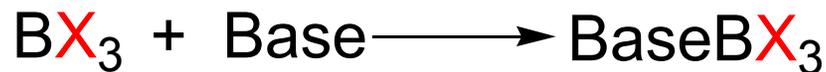
Important Goals: (1) high yields, (2) avoid the formation of B-O bonds, (3) avoid the formation of B₂H₆, and (4) recover all products

First Step: Digestion of Spent Fuel by Super Acidic Halo-Acids

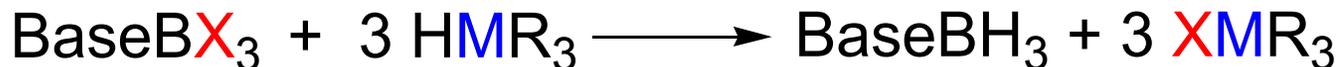


Second Step: One-Pot Conversion of BX₃ to AB

Coordination of BX₃



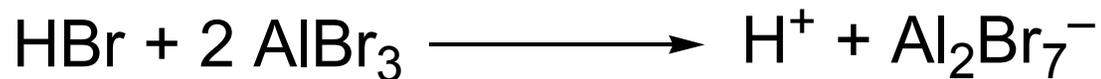
BX Reduction



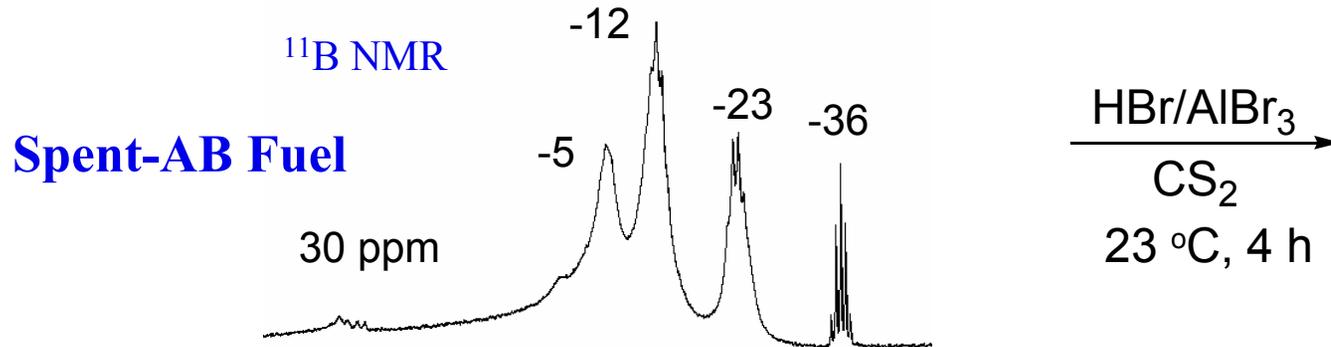
Base Displacement by NH₃ Yields AB



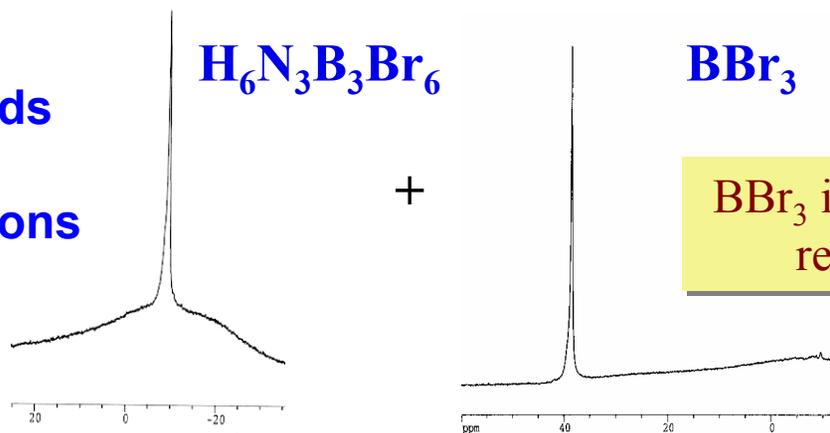
2007: Step 1. Digestion. Superacidic HX/AlX₃ Solutions Digest BNH_x Spent-Fuels



Farcasiu, D.; Fisk, S. L.; Melchior, M. T.; Rose, K. D. *J. Org. Chem.* **1982**, *47*, 453-7



Product ratio depends upon spent-fuel reactants and conditions

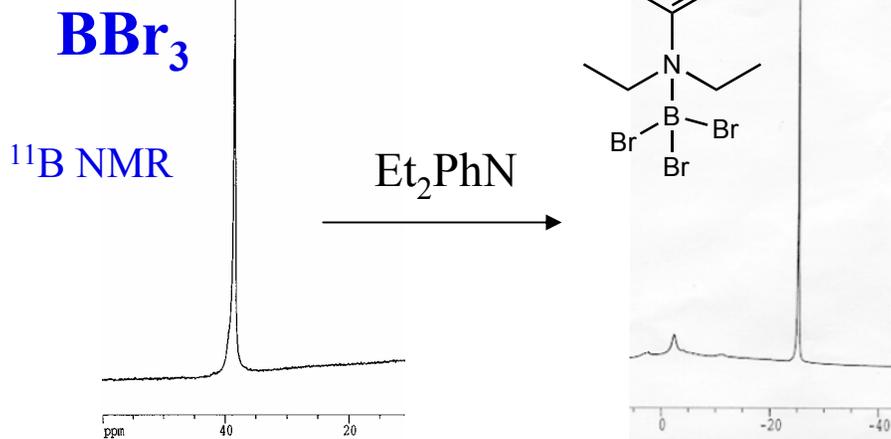


BBr_3 is distilled from the reaction mixture

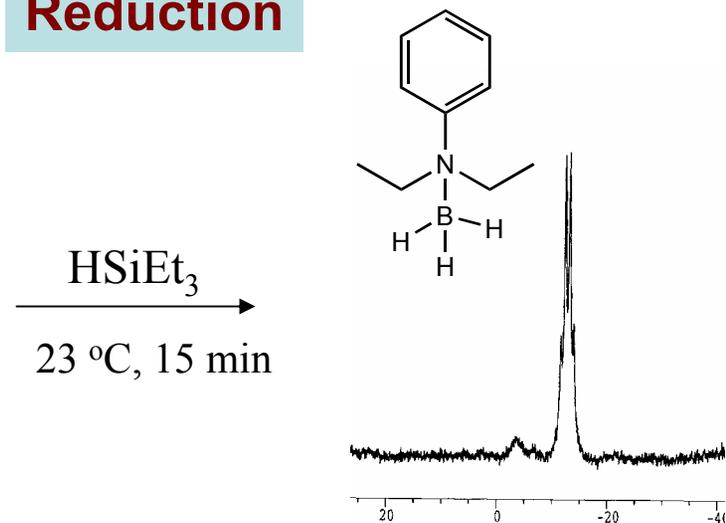
2007: Step 2. Coordination, Reduction and Displacement to Regenerate AB from BBr₃

A One-Pot 84%-Yield of AB from BBr₃ Has Been Achieved via the Reduction of Diethylaniline-BBr₃ Followed by NH₃ Exchange

Amine-Coordination

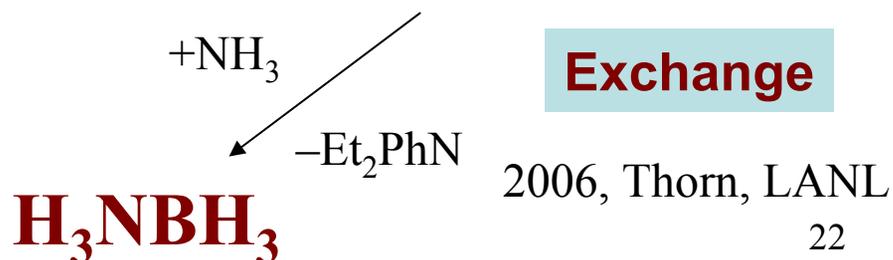


Reduction



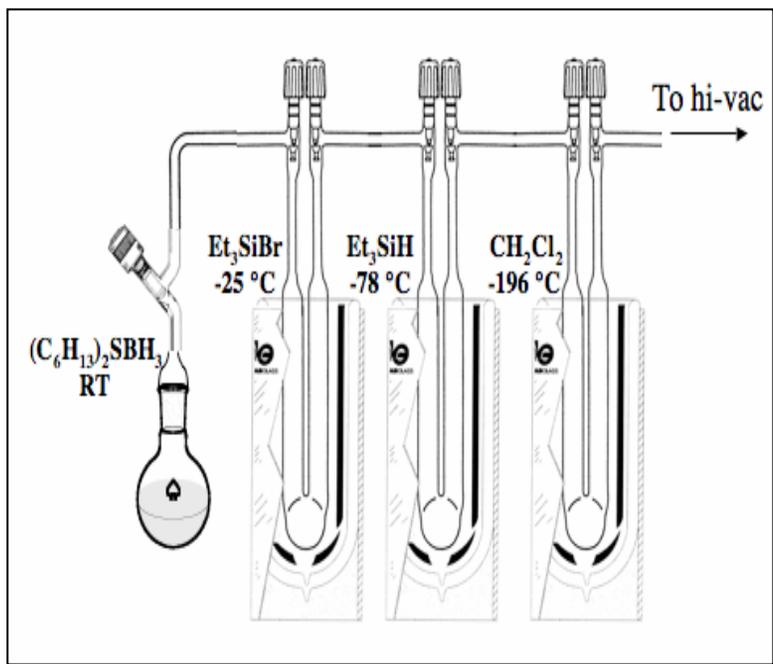
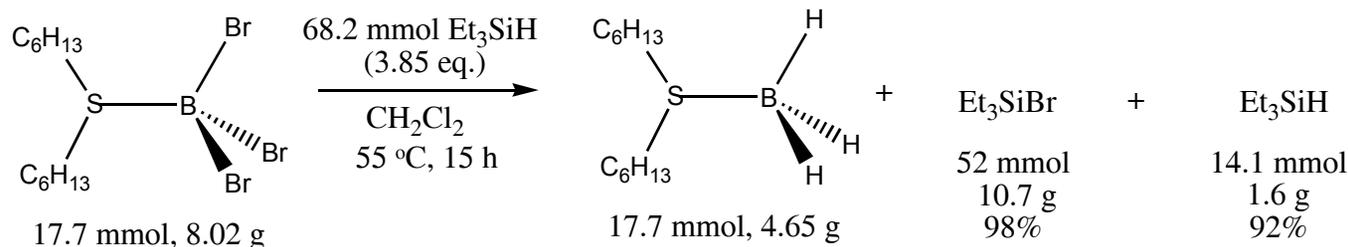
Alabama (Dixon) analysis indicates regeneration efficiency for total process (Steps 1 and 2) could meet 60% DOE target, depending upon reactants and heat recovery

Exchange

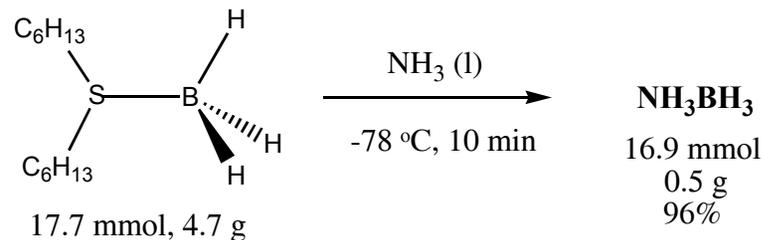


2008: New Reduction Processes are Quantitative and Allow Separation and Recovery of All Products

Reduction with Silane



Reaction with Ammonia

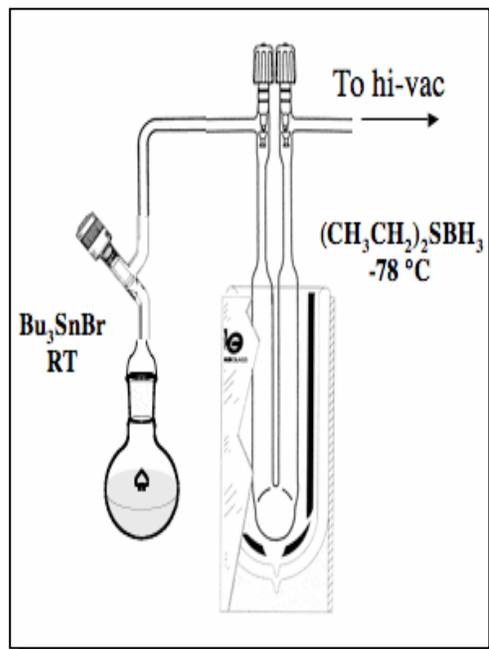
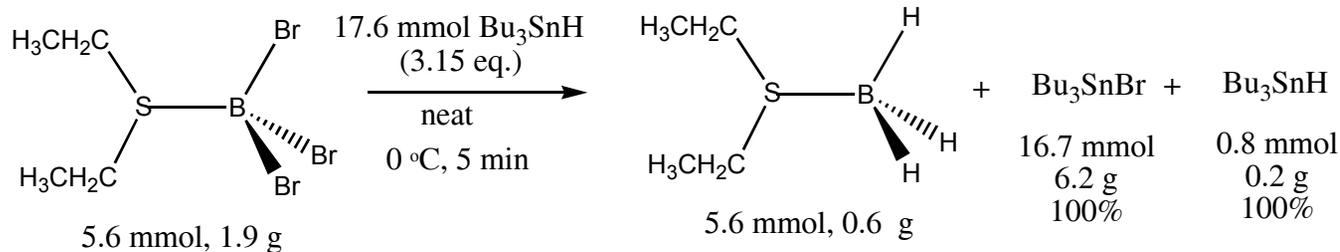


Residual ammonia is removed in-vacuo leaving a slurry of AB and hexylsulfide. Hexyl sulfide is removed by washing with hexane. AB is then collected and dried. Hexyl sulfide can be recovered by removing hexane in vacuo

Isolation of Reduction Products

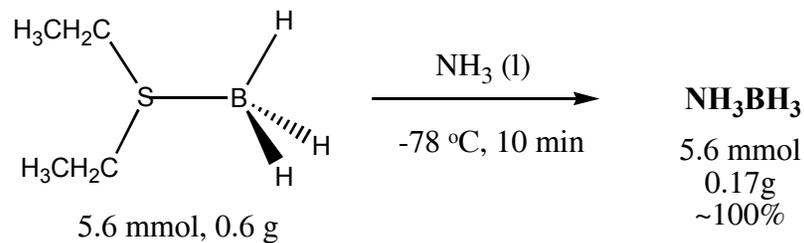
Overall AB Yield from BBr₃; 96%

Reduction with Stannanes



Isolation of Reduction Products

Reaction with Ammonia



Overall AB Yield from BBr₃: 100%

Both Procedures Avoid Handling B₂H₆

Future Studies

AB H₂-Release



AB and MAB Regeneration

- Optimize the higher-temperature/weight-ratios for ionic liquid based H₂-release systems
- Continue to develop and optimize chemical-promoter systems with improved H₂-release rates
- Investigate a wider range of metal catalysts for H₂-release in ionic liquids
- NMR studies focused on learning how to control H₂-release mechanisms to achieve the most regenerable spent fuels
- Take advantage of synergistic mechanisms to improve H₂-release rates

- **AB Digestion:** The conversion of spent fuel to BX₃ must be improved for this scheme to be viable. Future work will use more forcing conditions.
- **BX₃ Reduction:** This step is finished and optimized in the laboratory, but is it industrially feasible? Future collaborative work with Rohm and Haas will focus on process design and scalability.
- In collaboration with other center partners, new investigations of the use of the super-acid/halide-reduction process for the regeneration of other fuels such as LiNH₂BH₃.



DOE Hydrogen Program

Collaborations and Technology Transfer

Penn work on H₂-Release/Regeneration is Highly Coordinated with Partners by Frequent “Brainstorming” Discussions, Laboratory Visits, and Sample and Measurement-Sharing. Partner Collaborations Provide Complimentary Expertise:

- Penn:** new H₂-release methods for AB and AT using chemical promoters and ionic liquids; solution NMR-characterization and regeneration of spent-fuel products
- LANL:** AB homogeneous and acid dehydrogenation catalysts and regeneration methods
- PNNL:** supported AB dehydrogenation catalysts and studies of key dehydrogenation steps, new hydrogen-recovery methods, solid-state NMR studies
- U. of Washington:** studies of fundamental amineborane coordination chemistry and mechanisms of homogeneously catalyzed AB dehydrogenation
- U. of Alabama:** computational studies of amineborane reaction pathways and stabilities, evaluation of the energetics of regeneration methods
- Rohm and Haas:** provides starting materials for amineborane synthesis and key expertise in process design and scalability.

Future Studies will Now Rely Heavily on Industrial and National Laboratory Partners for Engineering and Scale-Up of Technologies

- PNNL and LANL:** Engineering assessments and implementation of solid and liquid-based H₂-release systems.
- Rohm and Haas:** Engineering assessment and scale-up of new regeneration process